

AD-A097 848

NAVAL AIR DEVELOPMENT CENTER WARMINSTER PA AIRCRAFT --ETC F/G 11/6
EFFECTS OF A MAGNETIC FIELD ON HYDROGEN EVOLUTION REACTION AND --ETC(U)
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NADC-81029-60

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REPORT NO. NADC-81029-60

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EFFECTS OF A MAGNETIC FIELD ON HYDROGEN EVOLUTION REACTION AND ITS DIFFUSION IN IRON AND STEEL

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March 10, 1981

PROGRESS REPORT

TASK AREA WR02201-001
Work Unit No. DG212

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Prepared for
NAVAL AIR SYSTEMS COMMAND
Department of the Navy
Washington, D. C. 20361

81 4 17 079

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(16) WR02201

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

NADC-81029-67

AD-A097848

(9)

EFFECTS OF A MAGNETIC FIELD ON HYDROGEN EVOLUTION
REACTION AND ITS DIFFUSION IN IRON AND STEEL.

4. TYPE OF REPORT & PERIOD COVERED

Progress Report

5. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

V. S. Agarwala and J. J. DeLuccia

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Naval Air Development Center
Aircraft and Crew Systems Technology Directorate
Warminster, PA 18974

10. PROGRAM ELEMENT, PROJECT, TASK

AREA & WORK UNIT NUMBERS
Program Element 61165N
Task Area WR02201001
Work Unit No. DG212

11. CONTROLLING OFFICE NAME AND ADDRESS

IR/IED Program
Naval Air Development Center
Warminster, PA 18974

12. REPORT DATE

11 10 March 1981

13. NUMBER OF PAGES

14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

(12) 20

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING
SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrogen charging	Magnetic domains
Magnetic field	Tafel slope
Hydrogen embrittlement	Liquid N ₂ temperature
Hydrogen permeation	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The presence of hydrogen in high strength steels results in catastrophic failure of a part much below its threshold strength. Chemical cleaning, finishing and electroplating processes generally introduce critical amounts of hydrogen in metals. In the present work an attempt has been made to retard hydrogen entry into the metal from such treatments by the use of a magnetic field. Experiments have shown that the effects of an applied magnetic field have affected both the hydrogen evolution reaction process and its diffusion in both Armco iron and high strength 4340 steel.

DD FORM 1473

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 3102-LF-314-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

393532

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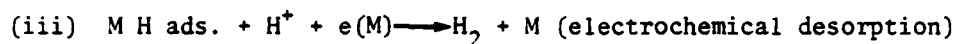
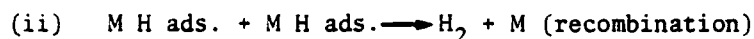
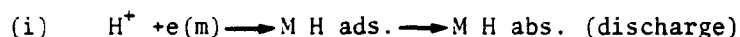
INTRODUCTION

Electroplating, acid pickling and electrochemical cleaning are processes that cause considerable hydrogen pick up in metals. In particular, cold headed fasteners, landing gear and other high strength load bearing steel structures or parts used in aircraft are normally chemically cleaned and electroplated with protective metals such as cadmium and nickel-chromium systems. During these treatments the high amount of hydrogen pick-up produces embrittlement (loss of ductility) in the alloy and under high stresses during service causes catastrophic failure of the component much below its nominal strength level. Recent studies have shown that less than a part per million of mobile atomic hydrogen was sufficient to cause failure of a high strength 4340 steel specimen at sustained loads even below 40% of the notched tensile strength (NTS) (reference a). Although bake-out procedures do remove some of the diffusible hydrogen from the metal parts, a very significant amount of mobile hydrogen can remain trapped in the bulk of the steel. The plated metal surface becomes a barrier for the exit of hydrogen from the underlying steel as hydrogen has a very low diffusivity in metals such as cadmium, chromium and nickel. The primary purpose of this investigation was to assess the possibility of retarding hydrogen entry into the steel from such treatments.

A method for retarding hydrogen entry into a metal must respond to the basic reaction mechanism by which hydrogen is produced at the metal/electrolyte interface and the processes by which it is transported to the bulk of the metal. In other words, the method should not only affect the hydrogen evolution reaction but also control the hydrogen absorption process in the metal. A magnetic field may affect the kinetics of both of these processes. It is believed that under the influence of a magnetic field, the magnetic domains of a metal arrange themselves in such a manner that both the charge-transfer reactions occurring at the interface, $H^+ + e \rightarrow H \text{ ads.}$, and the bulk diffusion of hydrogen into the metal, $H \text{ ads.} \rightarrow H \text{ abs.}$ can be affected. In particular, iron and steels (materials of high magnetic permeability) can easily order or align their magnetic domains to affect such changes.

There is very little work reported in the literature on the application of a magnetic field in electrochemical reactions. Only recently some papers have appeared which report activity in this area. Kelly reported that an applied magnetic field has an adverse effect on the corrosion resistance of the material. He showed that the interfacial potential of the corroding system moves to a more positive potential in the presence of a magnetic field and may enhance corrosion susceptibility of the metal (reference b). Relating to the electrochemical processes, the effects of a magnetic field have been reported to improve the results of electrothinning (reference c) and electrodeposition (reference d), altering the mass transport process of the reaction concerned. In other areas, the presence of a magnetic field has been reported to influence the fatigue life of a steel (reference e). The only evidence that hydrogen absorption is affected by the magnetic domains of the absorbing metal was in some Russian work (reference f). The investigators found that a close relationship exists between the intensity of the magnetic noise (Barkhausen Effect) and the concentration of the absorbed gas, which they suggested as quantitative and useful in monitoring hydrogen in the metal. So far there is no literature available where the effect of a magnetic field on the cathodic

processes of the hydrogen evolution reaction occurring at the metal/electrolyte interface has been investigated. The three partial reactions of the hydrogen evolution process



are the basic steps of hydrogen entry in metals and influence of a magnetic field could affect any of these reactions in both the magnitude (the kinetic aspects) and the rate controlling step in which case one reaction may be preferred (slow step) over the other. Therefore, a determination of the reaction that is influenced most by the magnetic domains of the metal was of interest in these investigations. A study has been made in which the effects of a magnetic field (of both low and high field strength) have been examined on both Armco iron and a high strength steel, AISI 4340 steel at the 1800-1930 MN/ $\frac{1}{2}$ level. The determination of electrochemical parameters of the hydrogen evolution reaction (h.e.r.) and that of hydrogen diffusion were made using electrochemical permeation methods (references g and h).

EXPERIMENTAL PROCEDURES

PERMEATION EXPERIMENTS

The schematic drawing of the electrochemical permeation cell and the circuit diagram of the instrumental set up are shown in Figure 1. The essential components of the cell were those of Devanathan and Stachurski (reference g). The present cell was modified only to accommodate attachment of two permanent magnets in either parallel or perpendicular directions to the plane of the specimen. The other details of the cell were the same as described elsewhere (reference i). Hydrogen was produced in the right side compartment by making the metal membrane (specimen) negative and the counter electrode (Pt) positive in a constant current mode circuit. The cathodic charging side of the membrane was termed the "input side." The other side of the membrane (left side compartment) was called the exit or extraction side and was connected to a potentiostat having a reference and a counter electrode. The electrolyte used in the charging cell was either 0.1 M H_2SO_4 solution or 0.1M NaOH + 0.2 M NaCN solution which was pre-deoxygenated. The cell on the exit side was filled with 0.1 M NaOH solution which was also deoxygenated. For most purposes the NaOH + NaCN system was sufficient to produce atomic hydrogen cathodically.

The specimens for permeation experiments were 2.5 cm squares of Armco iron cut from a hot rolled 1 mm thick sheet and were annealed to 480°C for one hour to remove residual stresses. Each side of the specimens was dry polished with 600 grit carbimet paper, chemically cleaned in 2% HCl/methyl alcohol solution for one minute, rinsed in methyl alcohol and air dried. One side of each specimen was plated with palladium by electroless plating in Pallamorse solution. A very thin film of palladium on iron was required to protect the specimen from corrosion during anodic polarization.

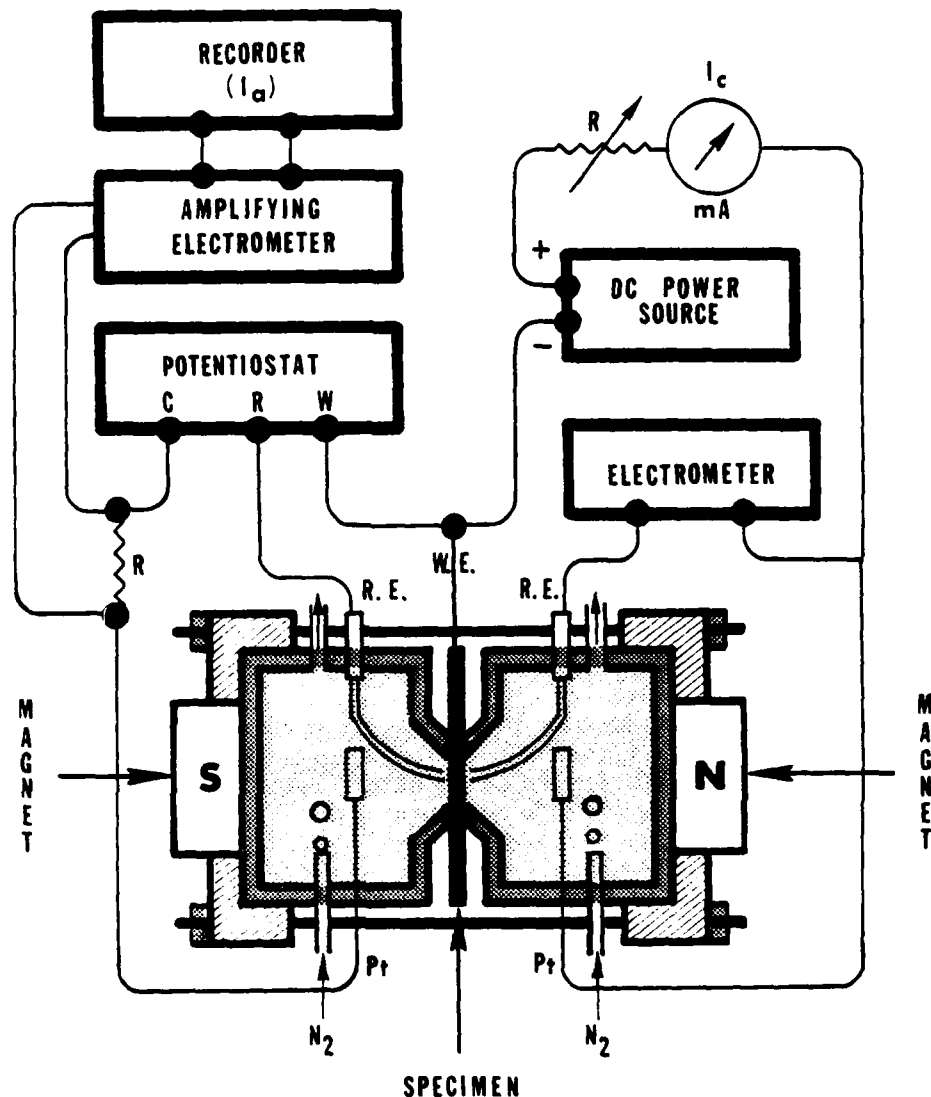


Figure 1. Schematic Representation of the Electrochemical Permeation Cell and the Circuit Diagram.

The experimental procedure for the permeation experiments was in the following order: The cell was set up as shown in Figure 1 and the electrolyte was added in the exit side cell. The specimen was potentiostated to a potential just above (noble) the rest potential of Pd/0.1 M NaOH solution and the anodic current (I_a) was recorded. When a steady state anodic current ($0 < I_a < 0.1 \mu\text{A}$) was reached, two permanent magnets were attached on either side of the specimen. These magnets were 2.5 cm squares of Co-Sm alloy with a field strength of 10,000 Oersted. Next, the electrolyte, 0.1 M NaOH + 0.2 M NaCN solution, was added in the top cell (input side) and while the I_a was recorded on the chart paper at the exit side, the specimen was connected to the negative terminal of a constant current device and the specimen was charged with hydrogen

at a predetermined cathodic current density, I_c . As soon as absorbed hydrogen appears at the other side of membrane (Armco iron specimen) it is immediately ionized to protons (H^+) and thus the permeation current, I_a , starts increasing and after a certain time reaches a steady state. The breakthrough time is the time elapsed from the instant cathodic current is turned on at the input side to the instant an increase in permeation current at the exit side is recorded. Such permeation measurements were made with and without the magnetic field applied to the cell and at several H-charging levels of cathodic current. The cathodic polarization measurements were also made to determine the effect of an applied magnetic field on the Tafel slope and exchange current density for the hydrogen evolution reaction.

EXPERIMENTS USING BARNACLE ELECTRODE MEASURING TECHNIQUE

In the experiments where very high field strength electromagnets were used, the limitations of the working area did not permit performance of regular permeation experiments. Therefore, an alternative method was used which has been recently developed in this laboratory (reference i). It is called the "Barnacle Electrode" method. It earned this name because the device can be attached to a structure for in situ determination of hydrogen. In this method the essentials of the permeation technique were the same with the exception that the power for ionization of hydrogen was a galvanic cell formed by coupling the specimen (iron or steel) and the driving nickel/nickel oxide electrode. This replaced the conventional potentiostat, the reference and the counter electrodes and was sufficient to provide an output of > 400 mV in 0.2 M NaOH solution. The nickel/nickel oxide is a fairly stable non-polarizable electrode and gives very reproducible results. It did not show any appreciable change in electrode potential even after a few repeat runs. In this barnacle set up the cathodic charging cell (the H input side) was eliminated because the specimens used for hydrogen measurement were usually pre-charged with hydrogen. The schematic of the barnacle cell and the instrumentation used are shown in Figure 2. The theory and the details of the measurements are given in reference (i).

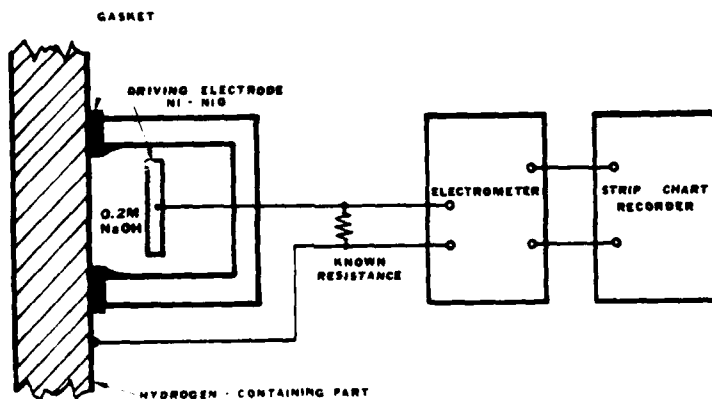


Figure 2. Schematic of the Barnacle Cell and the Related Circuit Diagram.

The barnacle experiments for determining diffusible hydrogen in iron and steel were made to study the effect of a high field magnet on hydrogen absorption (intake) during cathodic charging. The high field electromagnets used in these experiments were of 68,000 Oersted field strength with 2.5 cm. diameter and 15 cm. long working area in the center of the concentric discs of copper. The high field magnet (H.F.M.) facility used was provided by the High Field Magnet Laboratory of the Laboratory for Research on Structure of Matter of the University of Pennsylvania. The experiments performed in this high magnetic field consisted of charging the specimens with hydrogen at various cathodic current densities. The cell was comprised of a test tube 2.5 cm. in diameter and 24 cm. long and contained 0.1 M NaOH + 0.2 M NaCN solution as electrolyte. The experimental set up was as shown in Figure 3. The specimens for these experiments were 2.00 x 5.00 x 0.15 cm. in size for both the iron and steel. Except for a 10 cm² area, the rest of the area around the specimen was masked by a stop-off lacquer. Surface preparation consisted of abrasion with Scotch Brite, rinsing with alcohol and drying in air. A background measurement for hydrogen (using the barnacle method) was made on all specimens before any charging was done. This was to insure that all specimens had the lowest possible hydrogen level before starting the experiment. If necessary, they were degassed in a vacuum desiccator. The specimens of known hydrogen content were charged as described both in the presence and absence of H.F.M. They were then either stored in liquid nitrogen (temperature -196°C) immediately after removal from the charging cell for later determination of hydrogen, or were rinsed, Scotch Brite polished and clamped to the barnacle cell for immediate determination of hydrogen content in the metal.

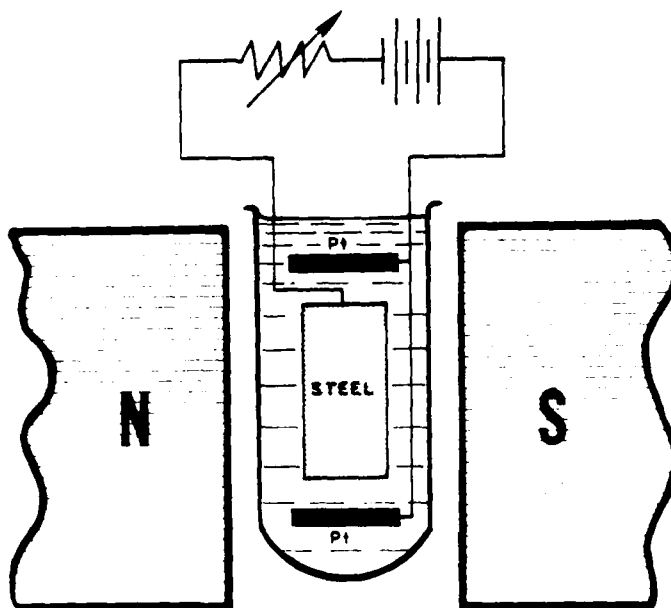


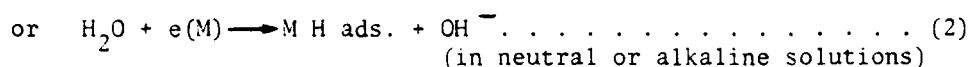
Figure 3. Schematic of the Apparatus for Hydrogen Charging of a Specimen in the High Magnetic Field.

The time durations in all these measurements were kept constant so that the kinetic factor of diffusion losses in room temperature atmosphere could be maintained consistently constant. In the experiments where cathodically charged specimens were maintained at low temperature (liquid nitrogen), the measurements of hydrogen were made after more than 20-hour storage and approximately 45 minutes warm-up to room temperature. The idea was to determine if there were any changes in H content after the metal had sufficient time to equilibrate its absorbed hydrogen within the bulk without any significant loss to the atmosphere.

RESULTS AND DISCUSSION

EFFECT ON HYDROGEN EVOLUTION REACTION

The overall process of electrolytic evolution of hydrogen mainly consists of two stages; (1) the discharge of hydrated protons to neutral hydrogen atoms



and (2) the desorption of hydrogen atoms from the cathode to the production of molecular hydrogen. It is this latter process that is of consequence in this study because the neutral hydrogen atoms adsorbed on the metal surface can diffuse into the bulk and cause embrittlement



Generally, it is believed that in the case of iron and steel, the rate determining step (slow step) of h.e.r. is the discharge step reactions (references j and k)(1) or (2). Under this kinetic mode the adsorbed hydrogen atoms have sufficient time to diffuse into the metal and cause embrittlement.

The results of the cathodic polarization measurements of Armco iron in 0.1 N H_2SO_4 are plotted in Figure 4. The values determined for Tafel slope, β , and the exchange current density, i_0 , were significantly decreased when a magnetic field was imposed on the system. For the Tafel relationship

$$\eta = \beta \log \frac{i}{i_0} \quad (4)$$

a decrease in i_0 generally corresponds to an increase in hydrogen over-voltage (η) provided the β value remains the same. In this particular instance the effect of a magnetic field has not only decreased i_0 but has also resulted in decreasing the value of β . In other words, the change in exchange current density may not necessarily be related to the change in hydrogen overvoltage.

Also, the concentration of adsorbed H atoms on the metal surface is so large ($\theta \approx 1$) that any concentration polarization effects due to diffusion of a very small number of H atoms through the metal could be eliminated. However, according to the Nernst equation where the term is equal to $\frac{-2.3RT}{\alpha F}$, α is the symmetry factor and F the Faraday constant, the decrease in Tafel slope from 120mV to 100mV measured from the cathodic polarization diagrams (cf Figure 4) is indicative of a change in α . Therefore, it is the symmetry factor that was changed by the magnetic field. For iron, α has been generally reported to be nearly 0.5. Assuming this to be the case, the value of α as calculated from the Nernst relation was found to be higher (0.6). The symmetry factor, α , is an intrinsic characteristic of the charge-transfer reaction of the h.e.r. at the interface. It denotes what fraction of the electrical energy affects the rate of electrochemical transformation when the potential of the interface is displaced from the equilibrium. In the present case an increase in α means the electrical energy barriers of charge transfer at the electrified interface are reduced such that the secondary discharges at the electrical double layer can much more easily occur. This can be translated as, the increase in α increases

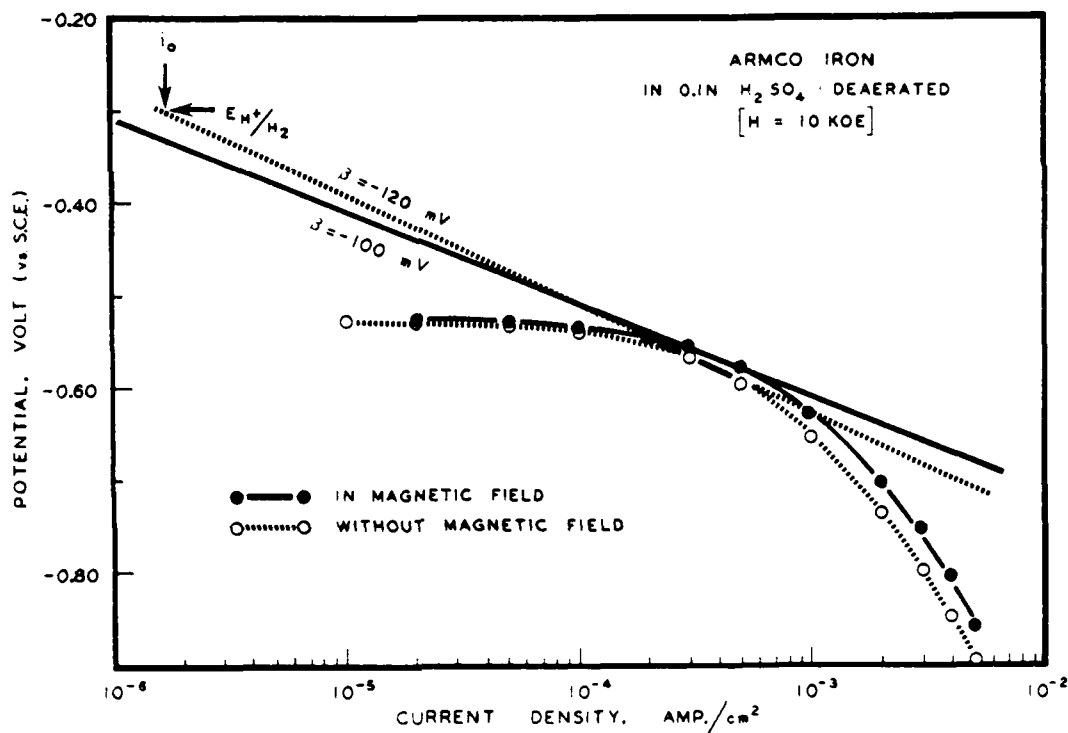


Figure 4. Cathodic Polarization Diagrams of Armco Iron in 0.1 N H₂SO₄ (Deaerated) both in Presence and Absence of a Magnetic Field.

the bond distance between the neutral H atom and the metal surface to such an extent that the recombination of atoms is easily accomplished. In other words, the desorption processes to form molecular hydrogen are favored. The mathematical details and the significance of α are better described elsewhere (reference 1). As an analogy it may be pointed out that noble metals like platinum or palladium favor recombination reactions in the hydrogen evolution process and are known to have high α values and low hydrogen overvoltage (lower Tafel slopes). According to Bonhoeffer (reference 2), these metals are catalytic to the h.e.r. and he suggested that the hydrogen recombination process was the predominant mechanism. When iron is subjected to a magnetic field, the magnetic domains of the metal create a surface effect such that the neutral H atoms gain some extra energy of activation to desorb from the metal surface and recombine to form molecular hydrogen.

EFFECT ON HYDROGEN DIFFUSION PARAMETERS

The result of the electrochemical permeation tests on Armco iron have shown that the breakthrough times for hydrogen to appear at the exit side of the specimen were longer when a magnetic field was imposed on the metal. Figure 5 shows a plot of these breakthrough times at different cathodic charging current densities on the input side of the specimen. The two curves demonstrate the shift of breakthrough times in the presence of a magnetic field.

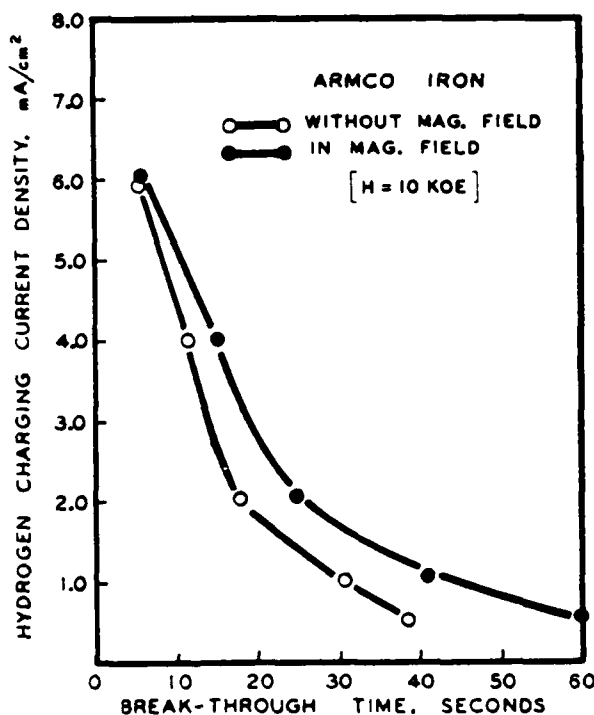


Figure 5. Effect of a Magnetic Field on Breakthrough Time t_b for Hydrogen Permeation Through Armco Iron and on the Hydrogen Charging Rate at the Input Side in 0.1 M NaCN + 0.1 M NaOH Solution.

Of particular interest in this plot was the effect of magnetic field vs. the charging currents. The differences in the breakthrough times with and without the magnetic field almost disappeared at very high H-charging cathodic currents (I_C). At lower I_C values (below 1.0 ma/cm^2) the presence of a magnetic field increases the breakthrough time, t_b , by over 30%. Similar observations were also made in the permeation currents recorded at the exit side. It was found that the $J_H (\text{max.})$, the maximum permeation current at the steady state, was lower in the presence of a magnetic field than in its absence (cf Figure 6). As the cathodic charging current density at the input side of the Armco iron specimen was increased, the differences due to the presence of a magnetic field gradually decreased. At cathodic current between 1 and 2 ma/cm^2 , the permeation currents (rates) for hydrogen were significantly affected by the magnetic field and were lower by almost 35%. However, at much lower values of I_C ($< 1.0 \text{ ma/cm}^2$) the differences in the permeation rates measured diminished. This was probably due to the difficulty found in measuring such low currents (less than $0.2 \mu\text{a}$) with high stability and reproducibility. At low charging currents the hydrogen diffusion through the metal should show much greater response under the imposed magnetic field. In the case of 4340 steel, the magnetic field showed a much

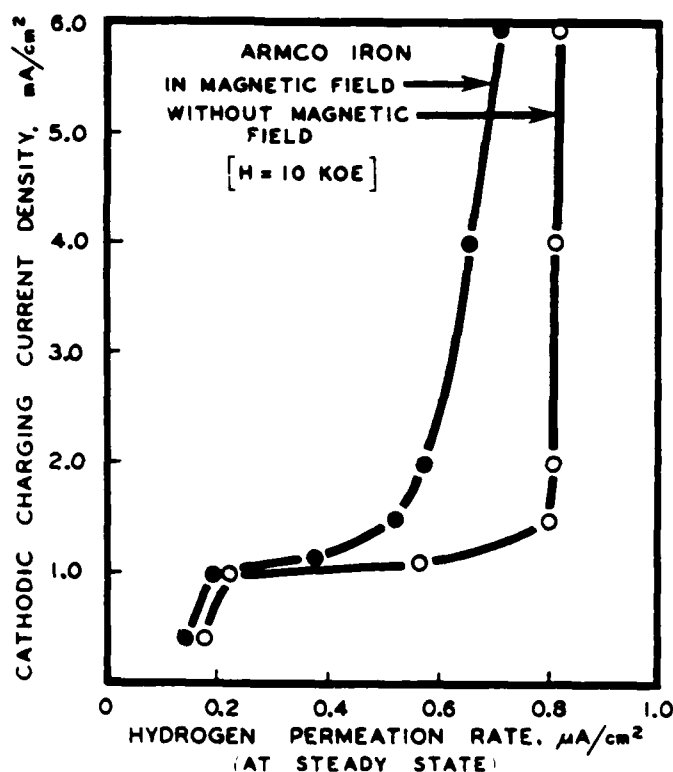


Figure 6. Plot of Hydrogen Permeation Current Density at Steady State Vs. the Hydrogen Charging Cathodic Current Density at Input Side for Armco Iron in the Presence and Absence of a Magnetic Field.

greater effect on hydrogen absorption in the bulk at lower charging currents (cf Figure 7). The decrease in the permeation current due to the presence of a magnetic field can occur in the following two ways: (1) less atomic hydrogen is present at the interface, and/or (2) the magnetic domains of the metal align themselves in such a way that H-diffusion through the bulk is somewhat restricted. In other words, the diffusivity of H in Armco iron could also decrease. However, it must be noted that the effect of a magnetic field is not very effective at very high rates of H-charging. As has been demonstrated in Figure 6, the permeation rate becomes almost independent of charging rate. At high hydrogen flux, the magnetic domains are probably not sufficiently strong enough to sustain the pressures of high fugacity of H at the metal interface. Some earlier works (references c, n and p) on the effect of hydrogen upon the magnetic properties of iron and mild steel strengthen this view. Coulson (reference n), Reber (reference o), and Kozloweski (reference p) have shown that hydrogen charging of iron and steel lowers their magnetic moments. They largely attributed the increase in hydrogen intake (absorption) to the decrease in magnetic moment.

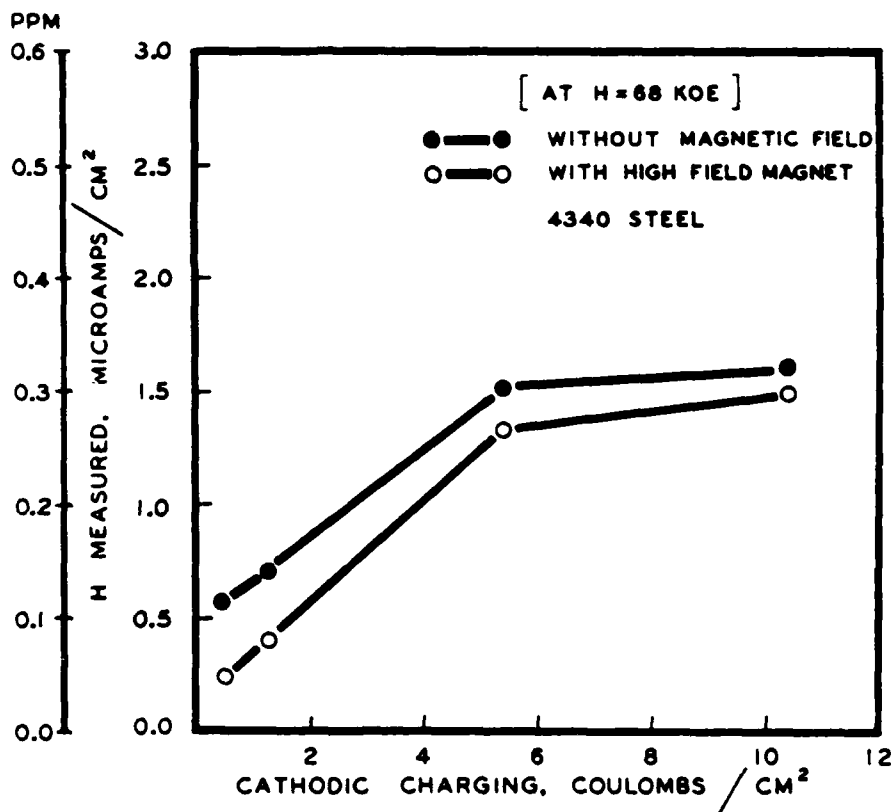


Figure 7. Effect of a High Magnetic Field on Hydrogen Intake in 4340 Steel During Cathodic Charging in 0.2 M NaCN + 0.2 M NaOH Solution.

The results of the experiments performed on both the iron and steel under a very high magnetic field (approximately 68 Kilo Oersted) have been summarized in Table I. They show that the amount of hydrogen absorbed in the metal during cathodic charging was significantly lower in the presence of the magnetic field. Thus, it may be concluded that the imposition of a high magnetic field may not only have compensated for the lowering of magnetic moment that results from cathodic charging (references n and p), but also created an additional barrier which helped retard the entry of hydrogen into the metal. It may be noted from Table I that entry of H in iron was much more impeded than in steel. This could be interpreted as due to the differences in the trapping locations of the two for hydrogen. In high strength steel such as AISI 4340, the trapping locations such as second phases, voids, inclusions, etc. are generally associated with multi-component systems. The plot in Figure 7 shows that at high cathodic charging, while the applied magnetic field was still very effective in inhibiting entry of hydrogen in Armco iron, the effectiveness was less significant for 4340 steel. This could be explained by the fact that under an externally applied magnetic field non-retentive high magnetically permeable substances like iron can be easily compensated for their loss of magnetic properties that result from hydrogen absorption in contrast to those characterized by high retention and low magnetic permeability such as 4340 steel. The high coercive forces for steel tend to keep the magnetic domains

TABLE I

Effect of High Magnetic Field on Absorption of
Hydrogen in Metals During Cathodic Charging

Metal	Cathodic Curr. Den. or H- Charging Rate, ma/cm ²	Cathodic Charging Time, Min.	Hydrogen Measured, $\mu\text{A}/\text{cm}^2$	
			Without Magnetic Field	In High Magnetic Field
Armco- Iron (1)	0.9	25	3.6	1.8
	0.9	30	3.6	1.5
	0*	0	1.7	1.0
AISI 4340 Steel (2)	4.0	45	1.6	1.45
	2.0	45	1.5	1.35
	0.9	25	0.7	0.4
	0*	0	0.3	0.2

(1) 5 min. reading of Barnacle Measurement for hydrogen

(2) 30 min. reading of Barnacle Measurement for hydrogen

* No cathodic charging, specimen was allowed to remain immersed in the test electrolyte for 30 min. Hydrogen pick-up from slight corrosion only.

of the metal immobile and therefore are not easily influenced by the external magnetic field. It may be also noted from Figure 7 that the permeation current of hydrogen measured above 50 coulombs/cm² for 4340 steel becomes independent of cathodic charging. The retardation effects of the applied magnetic field become almost insignificant at those high charging rates (above 10 coulombs/cm²). The second ordinate in Figure 7 also shows the calculated concentration levels of hydrogen present in the steel at various charging rates. They were determined by the barnacle method and calculated from the Laplace Transformed first term solution of the diffusion equation (reference j). Thus, in concentration terms a high magnetic field was able to retard hydrogen entry in steel up to 0.3 ppm of diffusible hydrogen. Considering that less than 0.1 ppm of diffusible hydrogen in this steel at below 40% N.T.S. can cause embrittlement failure (reference a), the inhibition offered by the magnetic field at those levels appears quite significant.

CONCLUSIONS

Significant changes in both the hydrogen evolution reaction and the diffusion parameters were found when Armco iron was cathodically charged in an electrolyte (0.05 M H₂SO₄ or 0.2 M NaCN + 0.1 M NaOH solutions) and exposed to a magnetic field. Under moderate charging conditions, (cathodic current densities of 1-2 ma/cm²), the breakthrough times for hydrogen to diffuse through the foil of Armco iron were found to be significantly delayed and the permeation currents measured at steady states were found to be approximately 25% lower when the magnetic field was present. The h.e.r. measurements showed a decrease in Tafel slope as well as the exchange current density indicating a slow discharge ($H^+ + e \rightarrow H$) and a fast recombination reaction thereby promoting molecularization of atomic hydrogen. The cathodic charging experiments performed on high strength 4340 steel under a very high field electromagnet (approximately 68 Kilo Oersted) showed a lower hydrogen intake in the metal and particularly at moderate charging currents ($i_c < 1 \text{ ma/cm}^2$). Hydrogen absorption in steel was reduced by almost 50% in the presence of a magnetic field. Thus, these investigations show that on application of a magnetic field during chemical cleaning and electroplating of steel, the effects of hydrogen embrittlement can be minimized and indications are that neither plating nor finishing qualities would be sacrificed (reference d).

The delay in the breakthrough time and a decrease in the permeation current due to hydrogen are direct results of the interference of the imposed magnetic field on the metal. It is suggested that under the influence of an external magnetic field the magnetic domains of the working metal are very strongly oriented in such a way that hydrogen entry is somewhat impeded. It probably counteracts the magnetic losses that are produced during cathodic charging and which allow hydrogen to absorb readily in the metal. Similar views were also held by Reber (reference o) and Kozlowski (reference p), who showed that hydrogen charging of iron and steel lowers the magnetic moment and permeability in the metal and increases its coercive force. In other words, the metal structure during charging becomes more complex creating several paths where hydrogen could remain trapped and not escape. An application of an external magnetic field compensates for these effects, less hydrogen is retained in the metal, and embrittlement is minimized.

FUTURE PLANNING

An extensive examination of the effect of a magnetic field on hydrogen absorption and permeation in iron and steel is planned. A very high field electromagnet will be used to carry out electrochemical permeation measurements and the use of cryogenic temperatures is envisaged to assure containment of the absorbed hydrogen in the metal. The anticipated pay-offs from this research work include: (1) avoiding excessive hydrogen pick-up by steel aircraft parts such as fasteners and landing gear during electroplating, and (2) increasing the reliability and life expectancy of naval aircraft from in service failures from hydrogen assisted cracking.

ACKNOWLEDGEMENT

The authors thank Drs. C. Grahame and T. Egami of L.R.S.M., the University of Pennsylvania for providing the facilities of the High Field Magnet Laboratory. The authors also wish to thank the Independent Research Board of the Naval Air Development Center for their generous financial support, Mrs. S. J. Ketcham for her helpful discussion and suggestions, and Mr. Kenneth Cenci for performing some experiments.

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